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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C07D 215/22, A01N 43/42, C07D 215/18, 401/06, 493/14 — A1

(11) International Publication Number: **WO 98/05646**

(43) International Publication Date: 12 February 1998 (12.02.98)

(21) International Application Number: PCT/US97/13089

(22) International Filing Date: 31 July 1997 (31.07.97)

(30) Priority Data:
60/022,906 1 August 1996 (01.08.96) US

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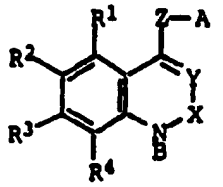
(81) Designated States: AL, AM, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, EE, GE, HU, IL, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, MD, MG, MK, MN, MW, MX, NO, NZ, PL, RO, RU, SD, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: 1,2-DIHYDROQUINOLINE DERIVATIVES HAVING FUNGICIDAL ACTIVITY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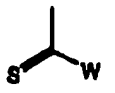
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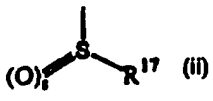
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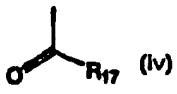
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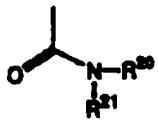
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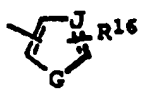
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(5a)

(57) Abstract

This invention provides compounds of formula (1) wherein X is CR^5, where R^5 is H, Cl or CH_3; Y is $CR^{5'}$ where $R^{5'}$ is H, Cl, or Br; Z is O, S, SO, SO_2, CH_2, CH_2CH_2, NR^6; B is (i, ii, iii, iv, or v) wherein s is 1 or 2, R^{17} is H, C_1-C_4 alkyl, C_1-C_4 acyl, CR^7R^8, where R^7 and R^8 are independently H, C_1-C_4 alkyl, C_1-C_4 alkenyl, C_2-C_4 alkynyl, or R^7 and R^8 together combine to form one or more optionally substituted carbocyclic rings containing four to six carbon atoms on each ring, and R^{20} and R^{21} are independently H, lower alkyl, cycloalkyl, optionally substituted phenyl, or $NR^{20}R^{21}$ together combine to form part of a saturated or unsaturated heterocyclic ring containing 1 to 3 nitrogen atoms; and A is (a) a C_1-C_{18} saturated or unsaturated straight or branched hydrocarbon chain, optionally including a hetero atom selected from O, S, SO, or SO_2, and optionally substituted with halo, halo C_1-C_4 alkoxy, OH, or C_1-C_4 acyl; (b) C_3-C_8 cycloalkyl or cycloalkenyl; (c) a phenyl group; (d) a furyl group; (e) a thienyl group; (f) a group of formula (5) or (5a); (g) a group selected from pyridyl or substituted pyridyl; (h) a group selected from pyrimidinyl or substituted pyrimidinyl; or (i) a group selected from 1-naphthyl, substituted 1-naphthyl, 4-pyrazolyl, 3-methyl-4-pyrazolyl, 1,3-benzodioxolyl, tricyclo[3.3.1.1(3,7)]dec-2-yl, 1-(3-chlorophenyl)-1H-tetrazol-5-yl, pyridyl, substituted pyridyl, or an acid addition salt of a compound of formula (1), or an N-oxide of a compound of formula (1) where Y is CH. The compounds of formula (1) are plant fungicides.

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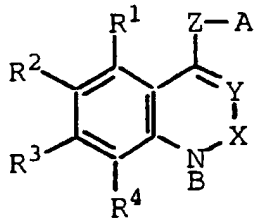
1,2-DIHYDROQUINOLINE DERIVATIVES HAVING FUNGICIDAL ACTIVITY

Background of the Invention

This invention provides novel compounds which are 1,2-dihydroquinoline derivatives having plant fungicidal activity. This invention also provides compositions and combination products containing one or more compounds of this invention as the active ingredient. Some of the combination products exhibit synergistic activity against plant pathogens. This invention also provides fungicidal methods.

Summary of the Invention

This invention provides novel compounds of formula (1)



(1)

wherein

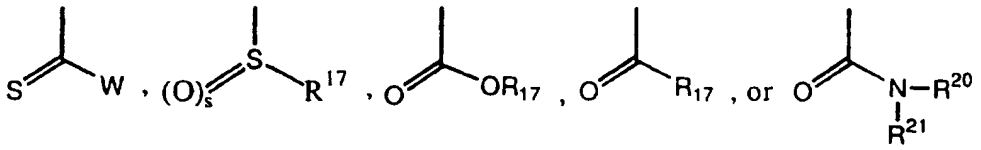
X is CR^5, where R^5 is H, Cl or CH_3;

Y is $CR^{5'}$ where $R^{5'}$ is H, Cl, or Br;

Z is O, S, SO, SO_2, CH_2, CH_2CH_2, NR^6, C_1-C_3 alkenyl, substituted C_1-C_3 alkenyl, $-CH_2O-$, $-OCH_2-$, OCH_2CH_2-, or $NR^6CH_2CH_2$, where R^6 is H, C_1-C_4 alkyl, C_1-C_4 acyl, CR^7R^8, where R^7 and R^8 are independently H, C_1-C_4 alkyl, C_1-C_4 alkenyl, C_2-C_4 alkynyl, C_1-C_4 acyl, CN, or OH, or R^7 and R^8 together combine to form a carbocyclic ring containing four to six carbon atoms;

R^1-R^4 are independently H, OH, NO_2, halo, I, C_1-C_4 alkyl, C_3-C_4 branched alkyl, C_1-C_4 alkoxy, halo C_1-C_4 alkyl, halo C_1-C_4 alkoxy, or halo C_1-C_4 alkylthio, or R^1 and R^2 or R^2 and R^3 together combine to form a carbocyclic ring containing four to six carbon atoms;

B is



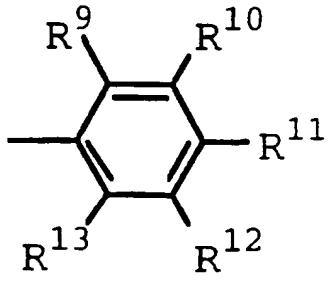
wherein s is 1 or 2, R^{17} is H, C_1-C_4 alkyl, C_1-C_4 acyl, CR^7R^8, where R^7 and R^8 are independently H, C_1-C_4 alkyl, C_1-C_4 alkenyl, C_2-C_4 alkynyl, or R^7 and R^8 together combine to form one or more optionally substituted carbocyclic rings containing four to six carbon atoms on each ring, and R^{20} and R^{21} are independently H, lower alkyl, cycloalkyl, optionally substituted phenyl, or $NR^{20}R^{21}$ together combine to form part of a saturated or unsaturated heterocyclic ring containing 1 to 3 nitrogen atoms; and

A is

(a) a C_1-C_{18} saturated or unsaturated straight or branched hydrocarbon chain, optionally including a hetero atom selected from O, S, SO, or SO_2, and optionally substituted with halo, halo C_1-C_4 alkoxy, OH, or C_1-C_4 acyl;

(b) C_3-C_8 cycloalkyl or cycloalkenyl;

(c) a phenyl group of formula (2)

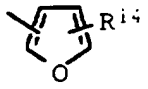


(2)

wherein

R^9-R^{13} are independently H, CN, NO_2, OH, halo, C_1-C_4 alkyl, C_3-C_4 branched alkyl, C_2-C_4 alkanoyl, halo C_1-C_7 alkyl, hydroxy C_1-C_7 alkyl, C_1-C_7 alkoxy, halo C_1-C_7 alkoxy, C_1-C_7 alkylthio, halo C_1-C_7 alkylthio, phenyl, substituted phenyl, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, phenyl C_1-C_4 alkyl, substituted phenyl C_1-C_4 alkyl, benzoyl, $SiR^{30}R^{31}R^{32}$ or $OSiR^{30}R^{31}R^{32}$, where R^{30} , R^{31}, and R^{32} are H, a C_1-C_6 straight chain or branched alkyl group, phenyl, or substituted phenyl, provided that at least one of R^{30}, R^{31}, and R^{32} is other than H, or R^{11} and R^{12} or R^{12} and R^{13} combine to form a carbocyclic ring, provided that unless all of R^9-R^{13} are H or F, then at least two of R^9-R^{13} are H;

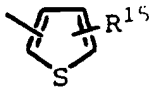
(d) a furyl group of formula (3)


(3)

wherein

R^{14} is H, halo, halomethyl, CN, NO_2, C_1-C_4 alkyl, C_3-C_4 branched alkyl, phenyl, or C_1-C_4 alkoxy;

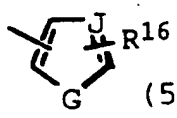
(e) a thienyl group of formula (4)


(4)

wherein

R^{15} is H, halo, halomethyl, CN, NO_2, C_1-C_4 alkyl, C_3-C_4 branched alkyl, phenyl, or C_1-C_4 alkoxy;

(f) a group of formula (5) or (5a)


(5)


(5a)

wherein

R^{16} is H, halo, halomethyl, CN, NO_2, C_1-C_4 alkyl, C_3-C_4 branched alkyl, phenyl, substituted phenyl, or C_1-C_4 alkoxy, and J is N or CH and G is O, NR^{19} or CH, provided that either J is N or G is NR^{19}, where R^{19} is H, C_1-C_4 alkyl, C_1-C_4 acyl, phenylsulfonyl, or substituted phenylsulfonyl;

(g) a group selected from pyridyl or substituted pyridyl;

(h) a group selected from pyrimidinyl or substituted pyrimidinyl; or

(i) a group selected from 1-naphthyl, substituted 1- naphthyl, 4-pyrazolyl, 3-methyl-4-pyrazolyl, 1,3-benzodioxolyl, tricyclo[3.3.1.1(3,7)]dec-2-yl, 1-(3-chlorophenyl)-1H-tetrazol-5-yl, pyridyl, substituted pyridyl, or an acid addition salt of a compound of formula (1), or an N-oxide of a compound of formula (1) where Y is CH.

Detailed Description of the Invention

Throughout this document, all temperatures are given in degrees Celsius and all percentages are weight percentages, unless otherwise stated.

The term halo, used alone or in combination with other terms, refers to F, Cl, or Br.

The term "alkyl" refers to a straight chain alkyl radical.

The term "branched alkyl" refers to all alkyl isomers containing the designated number of carbon atoms, except the straight chain isomers.

The term "alkoxy" refers to a straight or branched chain alkoxy group.

The term "halo alkyl" refers to a straight or branched alkyl group, substituted with one or more halo atoms.

The term "halo alkoxy" refers to an alkoxy group, substituted with one or more halo atoms.

The term "halo alkylthio" refers to a straight or branched alkylthio group, substituted with one or more halo atoms.

The term "acyl" refers to straight or branched chain alkanol.

The term "substituted phenyl" refers to phenyl substituted with up to three groups selected from halo, C_1-C_{10} alkyl, branched C_3-C_6 alkyl, halo C_1-C_7 alkyl, hydroxy C_1-C_7 alkyl, C_1-C_7 alkoxy, halo C_1-C_7 alkoxy, phenoxy, phenyl, NO_2, OH, CN, C_1-C_4 alkanoyloxy, or benzyloxy.

The term "substituted phenoxy" refers to a phenoxy group substituted with up to three groups selected from halo, C_1-C_{10} alkyl, branched C_3-C_6 alkyl, halo C_1-C_7 alkyl, hydroxy C_1-C_7 alkyl, C_1-C_7 alkoxy, halo C_1-C_7 alkoxy, phenoxy, phenyl, NO_2, OH, CN, C_1-C_4 alkanoyloxy, or benzyloxy.

The term "substituted phenylthio" refers to a phenylthio group substituted with up to three groups selected from halo, C_1-C_{10} alkyl, branched C_3-C_6 alkyl, halo C_1-C_7 alkyl, hydroxy C_1-C_7 alkyl, C_1-C_7 alkoxy, halo C_1-C_7 alkoxy, phenoxy, phenyl, NO_2, OH, CN, C_1-C_4 alkanoyloxy, or benzyloxy.

The term "substituted phenylsulfonyl" refers to a phenylsulfonyl group substituted with up to three groups

selected from halo, I, C_1-C_{10} alkyl, C_3-C_6 branched alkyl, halo C_1-C_7 alkyl, hydroxy C_1-C_7 alkyl, C_1-C_7 alkoxy, halo-C_1-C_7 alkoxy, phenoxy, phenyl, NO_2, OH, CN, C_1-C_4 alkanoyloxy, or benzyloxy.

The term "unsaturated hydrocarbon chain" refers to a hydrocarbon chain containing one to three multiple bond sites.

The term "carbocyclic ring" refers to a saturated or unsaturated ring of four to seven carbon atoms.

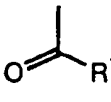
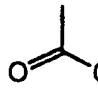
While all the compounds of this invention have fungicidal activity, certain classes of compounds may be preferred for reasons such as greater efficacy or ease of synthesis. These preferred classes include those compounds of formula (1), above, wherein:

X is CR^5 wherein R^5 is H;

Y is CR^5 wherein R^5 is H;

Z is O

R^1-R^4 are independently H, halo, or C_1-C_4 alkyl, or more preferably halo;

B is  or  wherein R^{17} is H, C_1-C_4 alkyl, CR^7R^8, where R^7 and R^8 are independently H, C_1-C_4 alkyl, C_1-C_4 alkenyl, C_2-C_4 alkynyl, or R^7 and R^8 together combine to form one or more optionally substituted carbocyclic rings containing four to six carbon atoms in each ring; and

A is a phenyl group of formula (2), above, wherein R^9R^{13} are independently halo or C_1-C_4 alkyl, or more preferably halo.

The compounds of formula (1) have been found to control fungi, particularly plant pathogens. When employed in the treatment or prevention of plant fungal diseases, the compounds are applied to seeds or plants in a disease-inhibiting and phytologically-acceptable amount. The term "disease-inhibiting and phytologically-acceptable amount", as used herein, refers to an amount of a compound of the invention which kills or inhibits the plant disease for which control is desired, but is not significantly toxic to the plant. This amount will generally be from about 1 to 1000 ppm, with 10 to 500 ppm being preferred. The exact concentration of compound required varies with the fungal disease to be controlled, the type of formulation employed, the method of application, the particular plant species, climate conditions, and the like. The compounds of this invention may also be used to protect stored grain and other non-plant loci from fungal infestation.

The following tests were performed to determine the fungicidal efficacy of the compounds of this invention.

Fungicide Utility

The compounds of the present invention have been found to control fungi, particularly plant pathogens. When employed in the treatment of plant fungal diseases, the compounds are applied to the plants in a disease inhibiting and phytologically acceptable amount. As used herein, the term "disease inhibiting and phytologically acceptable amount", refers to an amount of a compound of the present invention which kills or inhibits the plant disease for which control is desired, but is not significantly toxic to the plant. This amount will generally be from about 1 to 1000 ppm, with 10 to 500 ppm being preferred. The exact concentration of compound required varies with the fungal disease to be controlled, the type formulation employed, the method of application, the particular plant species, climate conditions and the like. A suitable application rate is

typically in the range from about 0.10 to about 4 lb/A. The compounds of the invention may also be used to protect stored grain and other non-plant loci from fungal infestation.

The following experiments were performed in the laboratory to determine the fungicidal efficacy of the compounds of the invention.

The test compounds were formulated for application by foliar spray. The following plant pathogens and their corresponding plants were employed.

Pathogen	Designation in following Table	Host
Erysiphe graminis tritici (powdery mildew)	PMW	wheat

Screening Method for PMW:

Wheat c.v. Monon was grown in the greenhouse from seed in a soil-less peat-based potting mixture ("Metromix"). The seedlings were used for testing at the 1.5 leaf stage. Compound formulation was accomplished by dissolving technical materials in acetone, with serial dilutions then made in acetone to obtain desired rates. Final treatment volumes were obtained by adding nine volumes 0.011% aqueous Triton X-100, resulting in test solutions with 10% acetone and 0.01% Triton X-100. Test rates were 400, 100, 25, and 6.25ppm.

In a high volume foliar application, plants were sprayed to runoff (using two opposing Spraying Systems 1/4JAUPM air atomization nozzles operated at approximately 138 kPa. Test inoculum for wheat powdery mildew (*E. graminis f. sp. tritici*) was produced *in vivo* on stock plants in the greenhouse. The test plants were inoculated by dusting spores from stock plants on test plants 24 hours after spray application

After inoculation the test plants were kept in the greenhouse for seven days, until disease on the untreated control plants was fully developed. Seven days after inoculation, the disease incidence on the leaves was assessed visually.

The following table presents the activity of typical compounds of the present invention when evaluated in these experiments. The effectiveness of test compounds in controlling disease was rated using the following scale.

NT	=	not tested against specific organism
0	=	0% control
-	=	1-49% control
+	=	50-100% control

COMPOUND NUMBER	RATE (ppm)	PMW
1	400	+
1	100	+
1	25	+
1	6.25	-
2	400	+
2	100	+
2	25	+
2	6.25	+
3	400	+
3	100	-
3	25	-
3	6.25	-
4	400	+
4	100	+
4	25	+
4	6.25	+
5	400	+
5	100	+
5	25	+
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15	100	+
15	25	-
15	6.25	-
16	400	+

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17	100	NT
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17	6.25	NT
18	400	+
18	100	NT
18	25	NT
18	6.25	NT
19	400	+
19	100	NT
19	25	NT
19	6.25	NT
20	400	-
20	100	NT
20	25	NT
20	6.25	NT

The compounds of this invention are made using well known chemical procedures. The required starting materials are commercially available, or readily synthesized utilizing standard procedures, several of which are disclosed in U.S. Patent 5,145,843. The compounds of formula (1) are then prepared by reduction of the corresponding quinolines with suitable reducing agents, such as, for example, diisobutylaluminium hydride, in a suitable solvent, such as, for example, ether, and subsequent acylation.

The following nonlimiting example further illustrates this invention.

Example 1

1-Methoxycarbonyl-5,7-dichloro-4-(4-fluorophenoxy)-1,2-dihydroquinoline

To a stirred suspension of 5,7-dichloro-4-(4-fluorophenoxy)-quinoline (0.62 gm, 2 mmol) in dry ether (10 ml) at room temperature was added a solution of diisobutylaluminium hydride (2.5 ml; 1M in THF). After 30 minutes, methyl chloroformate (0.5 ml) was added while cooling in ice, and the mixture was allowed to stand at room temperature 16 hours. Water was added followed by 1M HCl (4 ml) and the mixture was extracted with ether. Extracts were washed with saturated brine, dried with magnesium sulphate

and evaporated to a viscous oil which crystallized (0.75 gm, 100%). Recrystallisation from ether/hexane gave a colorless solid (mp 110°). Found: C: 55.66, H: 3.31, N: 3.55; $C_{17}H_{11}NCl_2FO_3$ requires: C: 55.61, H: 3.02, N: 3.81%. $\delta(CDCl_3)$ 3.84 (3H s, MeO), 4.29 (2H d J=5Hz, H-2), 5.35 (1H t J=5Hz, H-3), 6.94-7.05 (4H m , 4-fluorophenyl), 7.18 (1H d J=2Hz, H-6), 7.57 (1H br, H-8).

Example 2

5,7-Dichloro-4-(4-fluorophenoxy)-1,2-dihydroquinoline

To a stirred suspension of lithium aluminium hydride (Aldrich, 3.7 gm, 0.1 mole) in THF (250 ml) was added 5,7-dichloro-4-(4-fluorophenoxy)-quinoline (15.gm, 0.05 mole) in THF (100ml) giving a green color. The mixture was stirred for 1 hour then quenched with water (3.5 ml) in THF (10ml), then with 10M NaOH (3.5 ml) , and finally with water (3.5 ml) with cooling. The mixture was filtered and the filtrate evaporated to a viscous oil (15.05 gm, 97.1%) and stored at -20°. $\delta(CDCl_3)$ 4.05 (2H d, J=5Hz, H-2), 5.20 (1H t, J=5Hz, H-3), 6.44 (1H d, J=2Hz, H-6), 6.68 (1H d, J=2Hz, H-8), 6.90-7.05 (4H m , 4-fluorophenyl).

Example3

1-Acetyl-5,7-dichloro-4-(4-fluorophenoxy)-1,2-dihydroquinoline

To 5,7-dichloro-4-(4-fluorophenoxy)-1,2-dihydroquinoline (0.93 gm, 3.00 mmol) and triethylamine (2 ml) in dry dichloromethane (10 ml), cooled to -70°, was added acetyl chloride (0.3 ml, 4.2 mmol). The mixture was allowed to warm to ambient temperature over 2 hours then stood for 20 hours. Water was added, the organic phase separated, washed with brine and evaporated to an oil. Chromatography on flash silica, eluting with dichloromethane gave an oil (0.82 gm,77.6%). $\delta(CDCl_3)$ 2.28(3H s, CH_3CO),

4.33 (2H br, H-2), 5.39 (1H t, J=5Hz, H-3), 6.95-7.07 (4H m , 4-fluorophenyl), 7.27 (2H s, H-6,8).

Example 4

1-Trifluoroacetyl-5,7-dichloro-4-(4-fluorophenoxy)-1,2-dihydroquinoline

To 5,7-dichloro-4-(4-fluorophenoxy)-1,2-dihydroquinoline (1.55 gm, 5 mmol) and triethylamine (2.5 ml) in dry dichloromethane (25 ml), cooled to -70°, was added trifluoroacetic anhydride (1.3 ml, 10 mmol) over one minute. The mixture was allowed to warm to ambient temperature over 2 hours then stood for 20 hours. Water was added, the organic phase separated, washed with brine and evaporated to an oil which solidified (2.02 gm,99.5%) and recrystallized from hexane (m.p. 106.5°). $\delta(CDCl_3)$ 4.25 (2H br, H-2), 5.39 (1H t, J=5Hz, H-3), 6.98-7.10 (4H m, 4-fluorophenyl), 7.37 (1H d, J=2Hz, H-6), 7.64 (1H br, H-6).

Example 5

4-(3-(4-t-butylphenyl))propyl-8-fluoro-1,2-dihydroquinoline

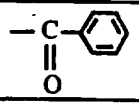
4-(3-(4-t-butylphenyl))propyl-8-fluoroquinoline (1.6g, 5mmol) was dissolved with stirring in dry THF (25mls) and a 1M solution of di-isobutylaluminium hydride (10mls, 10mmol) added dropwise. The mixture was heated under reflux conditions for sixteen hours and allowed to cool to room temperature. The mixture was quenched with saturated ammonium chloride and extracted with diethyl ether (2x100mls). The organic phase was washed with water and saturated brine and dried over anhydrous sodium sulphate. Evaporation of the solvent under reduced pressure and purification of the residue by chromatography gave the product (0.45g, 28%) as a cream solid, m.p. 90°C. (Found: C, 81.48; H, 8.37; N, 4.29%. $C_{22}H_{26}FN$ calculated: C, 81.69; H, 8.10; N, 4.33%)

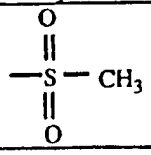
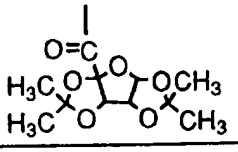
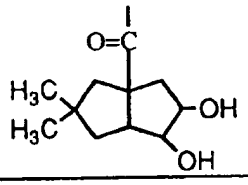
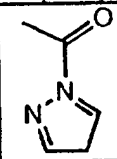
Example 6

1-(Pyrazoylcarbonyl)-4-(3-(4-t-Butylphenyl))propyl-8-fluoro-1,2-dihydroquinoline

4-(3-(4-t-Butylphenyl))propyl-8-fluoro-1,2-dihydroquinoline (0.44g, 1.37mmol) was slurried in dichloromethane (20mls) and triethylamine (0.42g, 4.11mmol) added dropwise. The mixture was cooled in ice and triphosgene (0.41g, 1.37mmol) was added in portions, solids dissolving to give a yellow solution. This was then stirred overnight, diluted with 1:2 ethyl acetate:hexane and filtered through silica, the product being eluted with 1:2 ethyl acetate:hexane. Evaporation of the solvent under reduced pressure gave the intermediate carbamoyl chloride (0.45g) as a cream, oily solid. The intermediate was dissolved in dichloromethane (25mls) and 4-dimethylaminopyridine (0.05g) and triethylamine (0.5g, 5mmol) added. Pyrazole (0.47g. 6.84mmol) was added and the mixture stirred overnight. The reaction mixture was adsorbed onto silica and the product eluted with 25-50% ethyl acetate:hexane. The desired product (0.32g, 56%) was isolated as a clear glass. (Found: C, 74.41; H, 7.27; N, 9.93%. $C_{26}H_{29}FN_3O$ calculated: C, 74.61; H, 6.98; N, 10.04%.)

The following Table identifies compounds of formula (1) prepared by the processes illustrated in the foregoing examples.

	Cmpd No.	R^1-R^4	B	R^5	$R^{5'}$	Z	A	M.P. (°C)
503583	1	5,7-diCl	$CO(OCH_3)$	H	H	O	4-flurophenyl	110
505280	2	5,7-diCl		H	H	O	4-flurophenyl	
505296	3	5,7-diCl	$CO(CC_4H_9)$	1-CH3-propyl	H	O	4-flurophenyl	
505297	4	5,7-diCl	$CO(CC_4H_9)$	H	H	O	4-flurophenyl	

505539	5	5,7-diCl	acetyl	H	H	O	4-flurophenyl	oil
506058	6	5,7-diCl		H	H	O	4-flurophenyl	
506479	7	5,7-diCl		H	H	O	4-flurophenyl	
512506	8	5,7-diCl	$CO(CF_3)$	H	H	O	4-flurophenyl	106.5
513316	9	5,7-diCl	CHO	H	H	O	4-flurophenyl	foam
513317	10	5,7-diCl		H	H	O	4-flurophenyl	
520247	11	5,7-diCl	$COC(CH_3)$	H	H	O	4-flurophenyl	
520248	12	5,7-diCl		H	H	O	4-flurophenyl	
520261	13	5,7-diCl		H	H	O	4-flurophenyl	
521878	14	5,7-diCl	$CO(OCH_3)$	CN	H	O	4-flurophenyl	166
521879	15	5,7-diCl	$CO(OCH_3)$	CH_3	H	O	4-flurophenyl	oil
521880	16	5,7-diCl	$CO(CH_3)$	CH_3	H	O	4-flurophenyl	oil
505152	17	8-F	H	H	H	C_2H_4	4-C(CH$_3$)$_3$phenyl	
505424	18	8-F	$COCH_3$	H	H	C_2H_4	4-C(CH$_3$)$_3$phenyl	glass
505425	19	8-F	COphenyl	H	H	C_2H_4	4-C(CH$_3$)$_3$phenyl	glass
505433	20	8-F		H	H	C_2H_4	4-C(CH$_3$)$_3$phenyl	glass

The compounds of this invention are applied in the form of compositions, which are important embodiments of the invention, and which comprise one or more compounds of formula (1) with a phytologically-acceptable inert carrier. The composition may optionally include fungicidal combinations which comprise at least 1% of one or more compounds of formula (1) with another fungicide.

The compositions are either concentrated formulations which are dispersed in water for application, or are dust or granular formulations which are applied without further

treatment. The compositions are prepared according to procedures which are conventional in the agricultural chemical art, but which are novel and important because of the presence therein of the compounds of this invention. Some description of the formulation of the compositions will, however, be given to assure that agricultural chemists can readily prepare any desired composition.

The dispersions in which the compounds are applied are most often aqueous suspensions or emulsions prepared from concentrated formulations of the compounds. Such water-soluble, water suspendable, or emulsifiable formulations are either solids usually known as wettable powders, or liquids usually known as emulsifiable concentrates or aqueous suspensions. Wettable powders, which may be compacted to form water dispersible granules, comprise an intimate mixture of the active compound, an inert carrier and surfactants. The concentration of the active compound is usually from about 10% to 90%. The inert carrier is usually chosen from among the attapulgite clays, the montmorillonite clays, the diatomaceous earths, or the purified silicates. Effective surfactants, comprising from about 0.5% to about 10% of the wettable powder, are found among the sulfonated lignins, the naphthalenesulfonates, alkylbenzenesulfonates, the alkyl sulfates, and non-ionic surfactants, such as, for example, ethylene oxide adducts of alkyl phenols.

Emulsifiable concentrates of the compounds comprise a convenient concentration of a compound, such as from about 10% to about 50% of liquid, dissolved in an inert carrier, which is either a water miscible solvent or a mixture of water-immiscible organic solvents, and emulsifiers. Useful organic solvents include aromatics, especially the high-boiling naphthalenic and olefinic portions of petroleum such as heavy aromatic naphtha. Other organic solvents may also be used, such as, for example, terpenic solvents, including rosin derivatives, aliphatic ketones, such as cyclkohexanone, and complex alcohols, such as 2-

ethoxyethanol. Suitable emulsifiers for emulsifiable concentrates are chosen from conventional nonionic surfactants, such as those mentioned above.

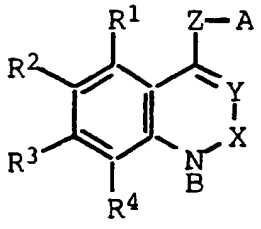
Aqueous suspensions comprise suspensions of water-insoluble compounds of this invention, dispersed in an aqueous vehicle at a concentration in the range from about 5% to about 50%. Suspensions are prepared by finely grinding the compound, and vigorously mixing it into a vehicle comprised of water and surfactants chosen from the same types discussed above. Inert ingredients, such as inorganic salts and synthetic or natural gums, may also be added, to increase the density and viscosity of the aqueous vehicle. It is often most effective to grind and mix the compound at the same time by preparing the aqueous mixture, and homogenizing it in an implement such as a sand mill, ball mill, or piston-type homogenizer.

The compounds may also be applied as granular compositions, which are particularly useful for applications to the soil. Granular compositions usually contain from about 0.5% to about 10% of the compound, dispersed in an inert carrier which consists entirely of in large part of clay or a similar inexpensive substance. Such compositions are usually prepared by dissolving the compound in a suitable solvent, and applying it to a granular carrier which a]has been pre-formed to the appropriate particle size, in the range of from about 0.5 to 3 mm. Such compositions may also be formulated by making a dough or past of the carrier and compound, and crushing and drying to obtain the desired granular particle.

Dusts containing the compounds are prepared simply by intimately mixing the compound in powdered form with a suitable dusty agricultural carrier, such as, for example, kaolin clay, ground volcanic rock, and the like. Dusts can suitably contain from about 1% to about 10% of the compound.

What is claimed is

1. A compound of formula (1)



(1)

wherein

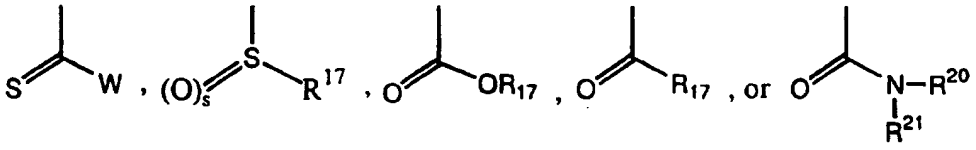
X is CR^5, where R^5 is H, Cl or CH_3;

Y is $CR^{5'}$ where $R^{5'}$ is H, Cl, or Br;

Z is O, S, SO, SO_2, CH_2, CH_2CH_2, NR^6, where R^6 is H, C_1-C_4 alkyl, C_1-C_4 acyl, CR^7R^8, where R^7 and R^8 are independently H, C_1-C_4 alkyl, C_1-C_4 alkenyl, C_2-C_4 alkynyl, C_1-C_4 acyl, CN, or OH, or R^7 and R^8 together combine to form a carbocyclic ring containing four to six carbon atoms;

R^1-R^4 are independently H, OH, NO_2, halo, I, C_1-C_4 alkyl, C_3-C_4 branched alkyl, C_1-C_4 alkoxy, halo C_1-C_4 alkyl, halo C_1-C_4 alkoxy, or halo C_1-C_4 alkylthio, or R^1 and R^2 or R^2 and R^3 together combine to form a carbocyclic ring containing four to six carbon atoms;

B is



wherein s is 1 or 2, R^{17} is H, C_1-C_4 alkyl, C_1-C_4 acyl, CR^7R^8, where R^7 and R^8 are independently H, C_1-C_4 alkyl, C_1-C_4 alkenyl, C_2-C_4 alkynyl, or R^7 and R^8 together combine to form one or more optionally substituted carbocyclic rings containing four to six carbon atoms on each ring, and R^{20} and R^{21} are independently H, lower alkyl, cycloalkyl, optionally substituted phenyl, or $NR^{20}R^{21}$ together combine to form part

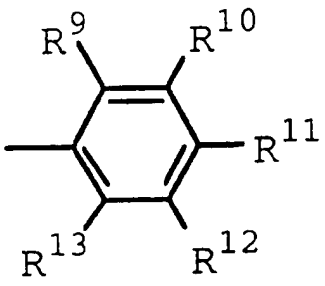
of a saturated or unsaturated heterocyclic ring containing 1 to 3 nitrogen atoms; and

A is

(a) a C_1-C_{18} saturated or unsaturated straight or branched hydrocarbon chain, optionally including a hetero atom selected from O, S, SO, or SO_2, and optionally substituted with halo, halo C_1-C_4 alkoxy, OH, or C_1-C_4 acyl;

(b) C_3-C_8 cycloalkyl or cycloalkenyl;

(c) a phenyl group of formula (2)

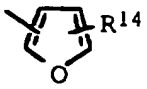


(2)

wherein

R^9-R^{13} are independently H, CN, NO_2, OH, halo, C_1-C_4 alkyl, C_3-C_4 branched alkyl, C_2-C_4 alkanoyl, halo C_1-C_7 alkyl, hydroxy C_1-C_7 alkyl, C_1-C_7 alkoxy, halo C_1-C_7 alkoxy, C_1-C_7 alkylthio, halo C_1-C_7 alkylthio, phenyl, substituted phenyl, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, phenyl C_1-C_4 alkyl, substituted phenyl C_1-C_4 alkyl, benzoyl, $SiR^{30}R^{31}R^{32}$ or $OSiR^{30}R^{31}R^{32}$, where R^{30} ,R^{31}, and R^{32} are H, a C_1-C_6 straight chain or branched alkyl group, phenyl, or substituted phenyl, provided that at least one of R^{30}, R^{31}, and R^{32} is other than H, or R^{11} and R^{12} or R^{12} and R^{13} combine to form a carbocyclic ring, provided that unless all of R^9-R^{13} are H or F, then at least two of R^9-R^{13} are H;

(d) a furyl group of formula (3)


(3)

wherein

R^{14} is H, halo, halomethyl, CN, NO_2, C_1-C_4 alkyl, C_3-C_4 branched alkyl, phenyl, or C_1-C_4 alkoxy;

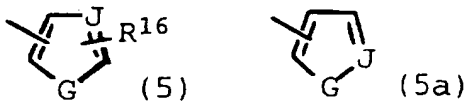
(e) a thienyl group of formula (4)


(4)

wherein

R^{15} is H, halo, halomethyl, CN, NO_2, C_1-C_4 alkyl, C_3-C_4 branched alkyl, phenyl, or C_1-C_4 alkoxy;

(f) a group of formula (5) or (5a)


(5) (5a)

wherein

R^{16} is H, halo, halomethyl, CN, NO_2, C_1-C_4 alkyl, C_3-C_4 branched alkyl, phenyl, substituted phenyl, or C_1-C_4 alkoxy, and J is N or CH and G is O, NR^{19} or CH, provided that either J is N or G is NR^{19}, where R^{19} is H, C_1-C_4 alkyl, C_1-C_4 acyl, phenylsulfonyl, or substituted phenylsulfonyl;

(g) a group selected from pyridyl or substituted pyridyl;

(h) a group selected from pyrimidinyl or substituted pyrimidinyl; or

(i) a group selected from 1-naphthyl, substituted 1- naphthyl, 4-pyrazolyl, 3-methyl-4-pyrazolyl, 1,3-benzodioxolyl, tricyclo[3.3.1.1(3,7)]dec-2-yl, 1-(3-chlorophenyl)-1H-tetrazol-5-yl, pyridyl, substituted

pyridyl, or an acid addition salt of a compound of formula (1), or an N-oxide of a compound of formula (1) where Y is CH.

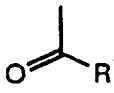
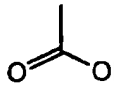
2. A compound of Claim 1 wherein

X is CR^5 wherein R^5 is H;

Y is CR^5 wherein R^5 is H;

Z is O

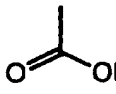
R^1-R^4 are independently H, halo, or C_1-C_4 alkyl;

B is  or  wherein R^{17} is H, C_1-C_4 alkyl, CR^7R^8, where R^7 and R^8 are independently H, C_1-C_4 alkyl, C_1-C_4 alkenyl, C_2-C_4 alkynyl, or R^7 and R^8 together combine to form one or more optionally substituted carbocyclic rings containing four to six carbon atoms in each ring; and

A is a phenyl group of formula (2), above, wherein R^9R^{13} are independently halo or C_1-C_4.

3. A compound of Claim 2 wherein

R^1-R^4 are independently halo;

B is  wherein R^{17} is H, C_1-C_4 alkyl, CR^7R^8, where R^7 and R^8 are independently H, C_1-C_4 alkyl, C_1-C_4 alkenyl, C_2-C_4 alkynyl, or R^7 and R^8 together combine to form one or more optionally substituted carbocyclic rings containing four to six carbon atoms in each ring; and

A is a phenyl group of formula (2), above, wherein R^9R^{13} is independently halo.

4. The compound 1-benzoyl-4-(4-fluorophenoxy)-5,7-dichloro-1,2-dihydroquinoline.

5. The compound 1-acetyl-4-(4-fluorophenoxy)-5,7-dichloro-1,2-dihydroquinloine.

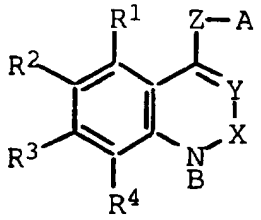
6. The compound 1-(methanesulphonyl)methylsulphonyl-4-(4-fluorophenoxy)-5,7-dichloro-1,2-dihydroquinoline.

7. The compound 1-trifluoroacetyl-4-(4-fluorophenoxy)-5,7-dichloro-1,2-dihydroquinoline.

8. The compound 1-formyl-4-(4-fluorophenoxy)-5,7-dichloro-1,2-dihydroquinoline.

9. The compound 1-(2,3:4,6-di-O-isopropylidene-2-keto-L-gulonyl)-4-(4-fluorophenoxy)-5,7-dichloro-1,2-dihydroquinoline.

10. A fungicidal method which comprises applying to the locus to be protected from fungus a fungicidally-effective amount of a compound of formula (1)



(1)

wherein

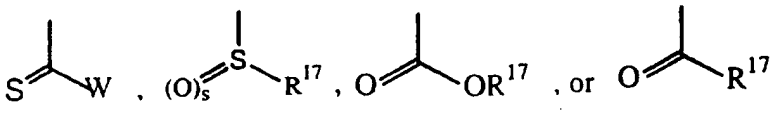
X is CR^5, where R^5 is H, Cl or CH_3;

Y is $CR^{5'}$ where $R^{5'}$ is H, Cl, or Br;

Z is O, S, SO, SO_2, CH_2, CH_2CH_2, NR^6, where R^6 is H, C_1-C_4 alkyl, C_1-C_4 acyl, CR^7R^8, where R^7 and R^8 are independently H, C_1-C_4 alkyl, C_1-C_4 alkenyl, C_2-C_4 alkynyl,

C_1-C_4 acyl, CN, or OH, or R^7 and R^8 together combine to form a carbocyclic ring containing four to six carbon atoms;

R^1-R^4 are independently H, OH, NO_2, halo, I, C_1-C_4 alkyl, C_3-C_4 branched alkyl, C_1-C_4 alkoxy, halo C_1-C_4 alkyl, halo C_1-C_4 alkoxy, or halo C_1-C_4 alkylthio, or R^1 and R^2 or R^2 and R^3 together combine to form a carbocyclic ring containing four to six carbon atoms;

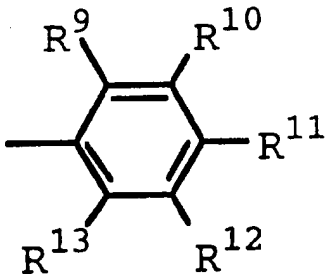
B is  wherein s is 1 or 2, and R^{17} is H, C_1-C_4 alkyl, C_1-C_4 acyl, CR^7R^8, where R^7 and R^8 are independently H, C_1-C_4 alkyl, C_1-C_4 alkenyl, C_2-C_4 alkynyl, or R^7 and R^8 together combine to form one or more optionally substituted carbocyclic rings containing four to six carbon atoms on each ring; and

A is

(a) a C_1-C_{18} saturated or unsaturated straight or branched hydrocarbon chain, optionally including a hetero atom selected from O, S, SO, or SO_2, and optionally substituted with halo, halo C_1-C_4 alkoxy, OH, or C_1-C_4 acyl;

(b) C_3-C_8 cycloalkyl or cycloalkenyl;

(c) a phenyl group of formula (2)



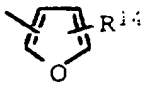
(2)

wherein

R^9-R^{13} are independently H, CN, NO_2, OH, halo, C_1-C_4 alkyl, C_3-C_4 branched alkyl, C_2-C_4 alkanoyl, halo C_1-C_7

alkyl, hydroxy C_1-C_7 alkyl, C_1-C_7 alkoxy, halo C_1-C_7 alkoxy, C_1-C_7 alkylthio, halo C_1-C_7 alkylthio, phenyl, substituted phenyl, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, phenyl C_1-C_4 alkyl, substituted phenyl C_1-C_4 alkyl, benzoyl, $SiR^{30}R^{31}R^{32}$ or $OSiR^{30}R^{31}R^{32}$, where R^{30} ,R^{31}, and R^{32} are H, a C_1-C_6 straight chain or branched alkyl group, phenyl, or substituted phenyl, provided that at least one of R^{30}, R^{31}, and R^{32} is other than H, or R^{11} and R^{12} or R^{12} and R^{13} combine to form a carbocyclic ring, provided that unless all of R^9-R^{13} are H or F, then at least two of R^9-R^{13} are H;

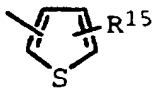
(d) a furyl group of formula (3)


(3)

wherein

R^{14} is H, halo, halomethyl, CN, NO_2, C_1-C_4 alkyl, C_3-C_4 branched alkyl, phenyl, or C_1-C_4 alkoxy;

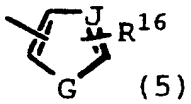
(e) a thienyl group of formula (4)

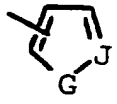

(4)

wherein

R^{15} is H, halo, halomethyl, CN, NO_2, C_1-C_4 alkyl, C_3-C_4 branched alkyl, phenyl, or C_1-C_4 alkoxy;

(f) a group of formula (5) or (5a)


(5)


(5a)

wherein

R^{16} is H, halo, halomethyl, CN, NO_2, C_1-C_4 alkyl, C_3-C_4 branched alkyl, phenyl, substituted phenyl, or C_1-C_4 alkoxy,

and J is N or CH and G is O, NR^{19} or CH, provided that either J is N or G is NR^{19}, where R^{19} is H, C_1-C_4 alkyl, C_1-C_4 acyl, phenylsulfonyl, or substituted phenylsulfonyl;

(g) a group selected from pyridyl or substituted pyridyl;

(h) a group selected from pyrimidinyl or substituted pyrimidinyl; or

(i) a group selected from 1-naphthyl, substituted 1- naphthyl, 4-pyrazolyl, 3-methyl-4-pyrazolyl, 1,3-benzodioxolyl, tricyclo[3.3.1.1(3,7)]dec-2-yl, 1-(3-chlorophenyl)-1H-tetrazol-5-yl, pyridyl, substituted pyridyl, or an acid addition salt of a compound of formula (1), or an N-oxide of a compound of formula (1) where Y is CH.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/13089

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D215/22 A01N43/42 C07D215/18 C07D401/06 C07D493/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	FR 2 183 194 A (MONROY H.) 14 December 1973 see claims ---	1,10
A	EP 0 173 208 A (NIHON TOKUSHU NOYAKU SEIZO K.K.) 5 March 1986 see claims ---	1,10

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search	Date of mailing of the international search report
25 November 1997	18/12/1997

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Van Bijlen, H

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/13089

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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